Electronic Supplementary Material (ESI) for Soft Matter.

Supplementary Information

for

Molecular Dynamics and Crystallization in Polymers based on Ethylene Glycol Methacrylates (EGMA) with Melt Memory Characteristics: from Linear Oligomers to Comb-like Polymers

Olga Vassiliadou,[a] Varvara Chrysostomou,[b] Stergios Pispas,[b] Panagiotis A. Klonos,[a] and Apostolos Kyritsis,[*,a]

[a] *Department of Physics, National Technical University of Athens, Zografou Campus, 15780, Athens, Greece*

[b] *Theoretical and Physical Chemistry Institute, National Hellenic Research Foundation, 48 Vassileos Constantinou Avenue, 11635 Athens, Greece*

**Corresponding author: akyrits@central.ntua.gr*

S1. Additional DSC data

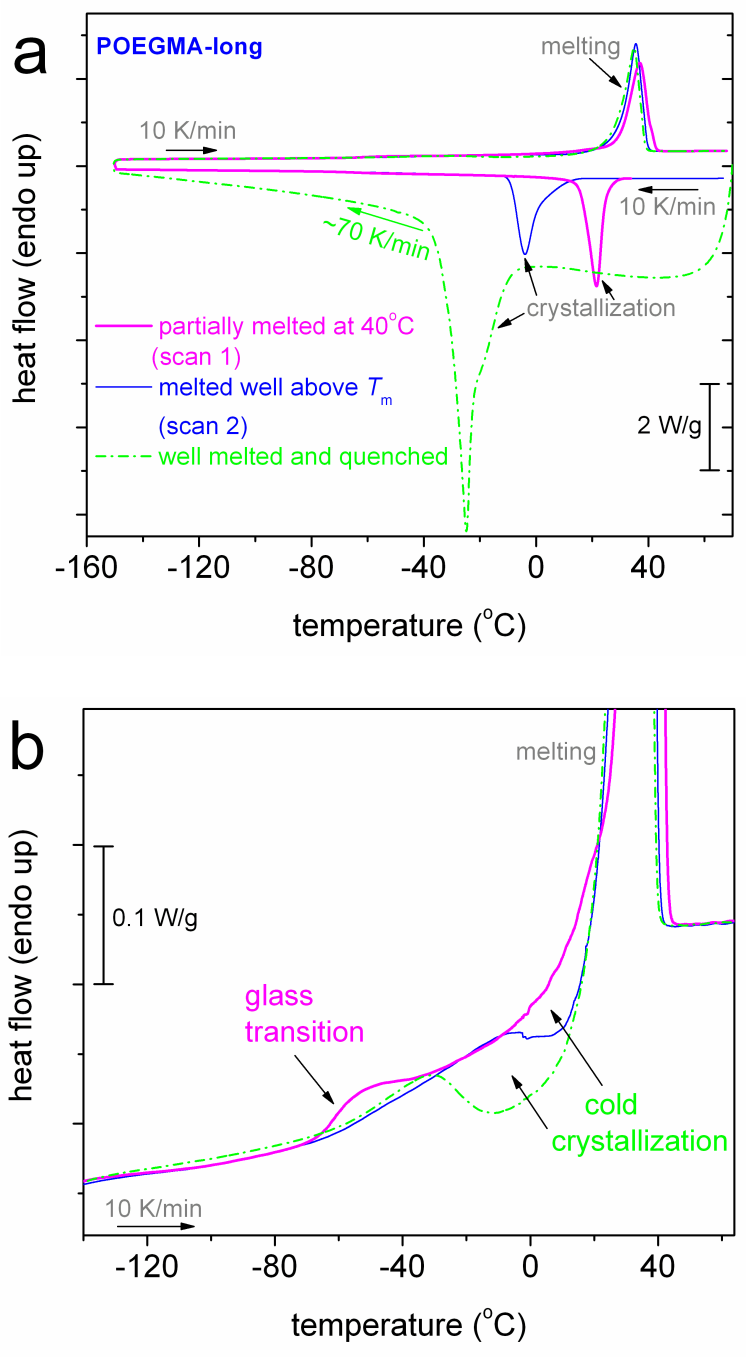

Figure S1. (a) DSC cooling/heating thermograms for POEGMA-long comparatively for different scans. (b) shows in more detail the heating thermograms focusing on the region of glass transition.

S2. Additional BDS data

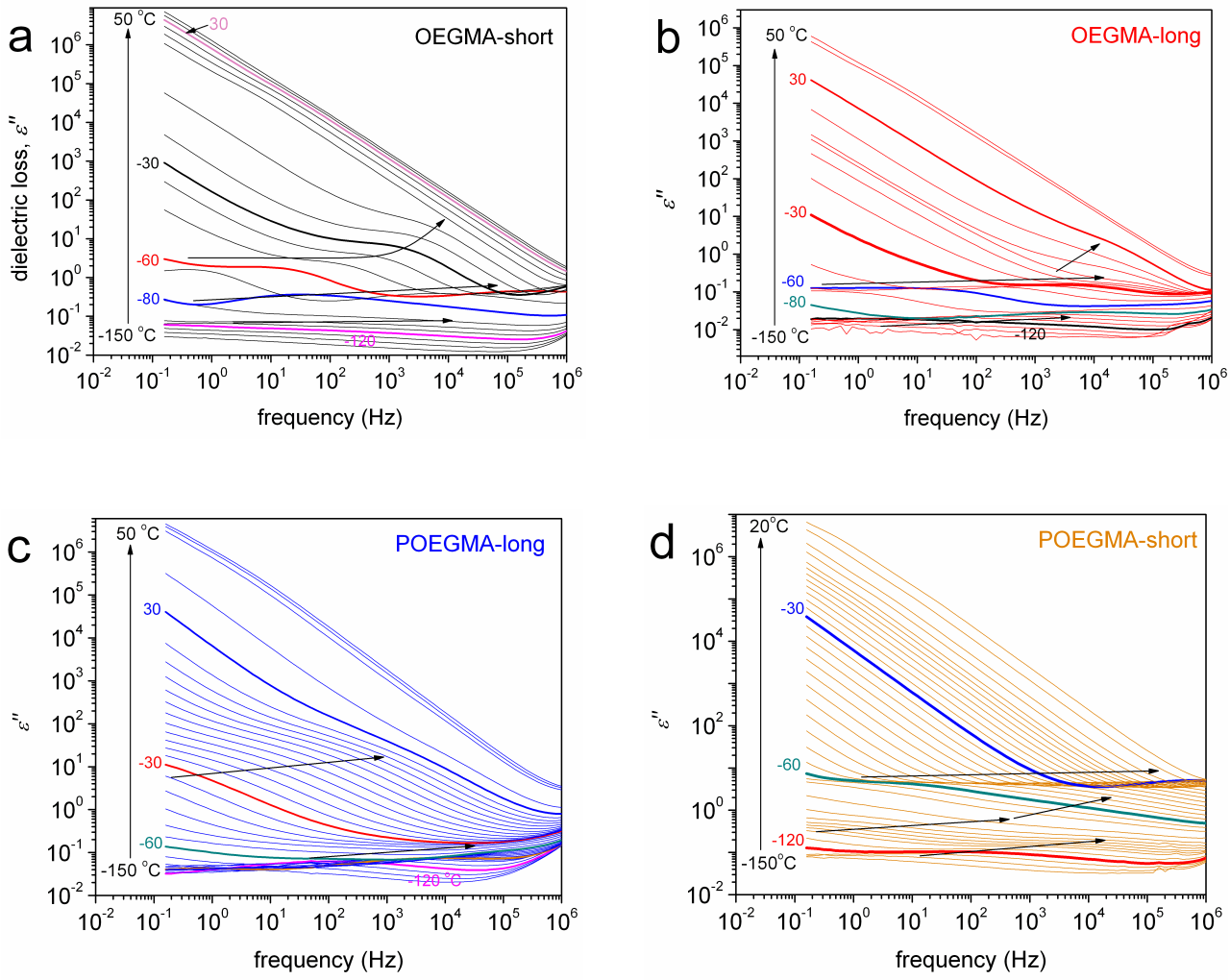

Figure S2. Isothermal BDS plots for the imaginary part of dielectric permittivity, ε'' (dielectric loss), for all samples and temperatures during 1st BDS scan. Data at selected temperatures have been marked by different colours to denote the different regions of local (lower *T*) and segmental (higher *T*) dynamics, furthermore, ionic conductivity effects. The added arrows mark roughly the recorded relaxations.

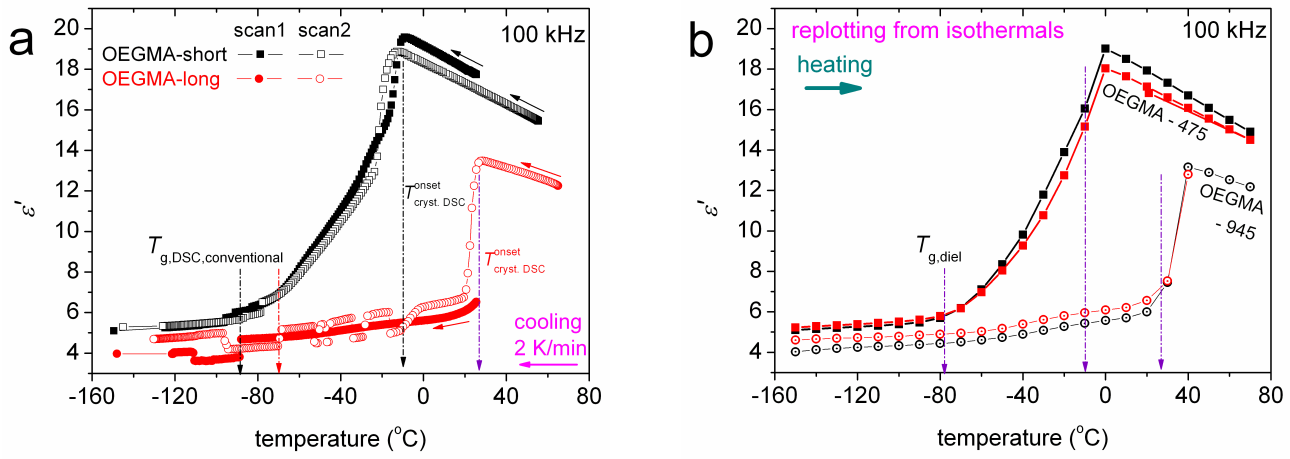

Figure S3. (a) BDS data in the form of isochronal plots of ε'' against temperature during continuous cooling at 2 K/min (ramps) for the fixed frequency of 100 kHz. (b) Isochronal replottings of measurements during heating at steps of 5 and 10 K (isothermals) at 100 kHz. Indicated are the calorimetric T_g, and the temperature of the crystallization initiation (onset).

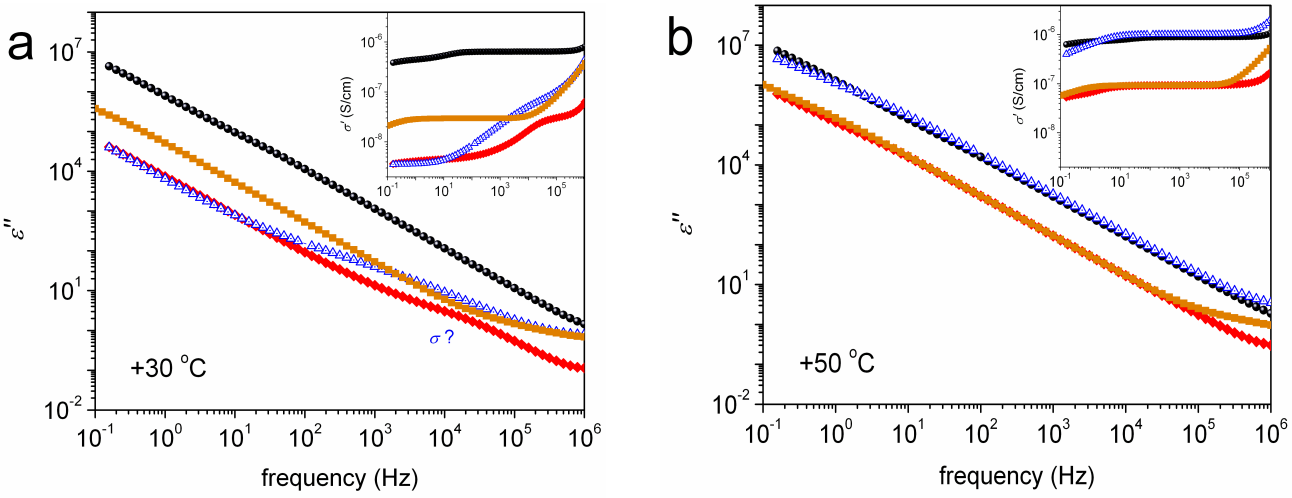

Figure S4. Isothermal BDS results of ε'' against frequency for all samples at the relatively high temperatures, >>T_g, of (a) 30 °C and (b) 50 °C. The insets present the respective results for the real part of conductivity, σ'.

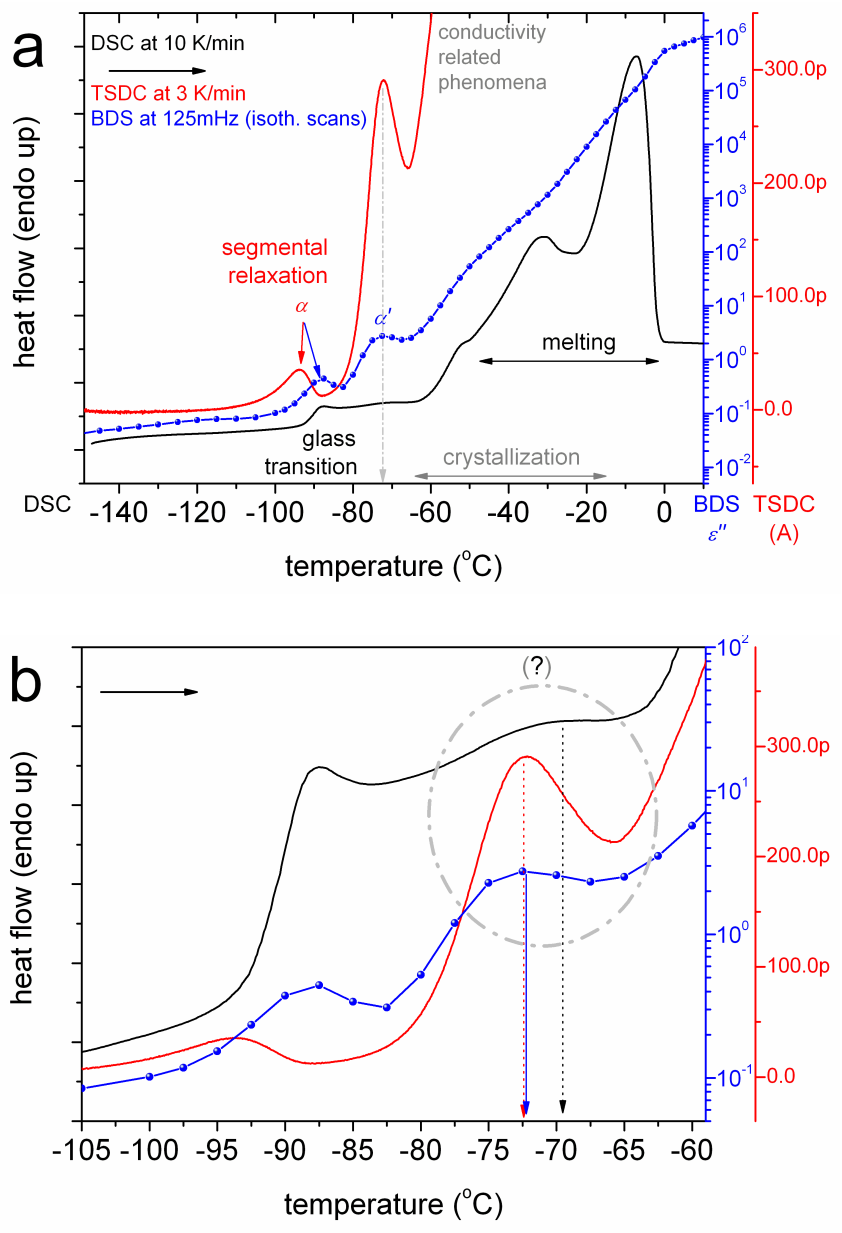

Figure S5. Comparative results between the employed techniques, namely DSC (heat flow), BDS (ε´´) and TSDC (current), in the form of temperature dependence the recorded variable during heating, (a) in the overall temperature range and (b) with focus on the temperature range of the glass transition.

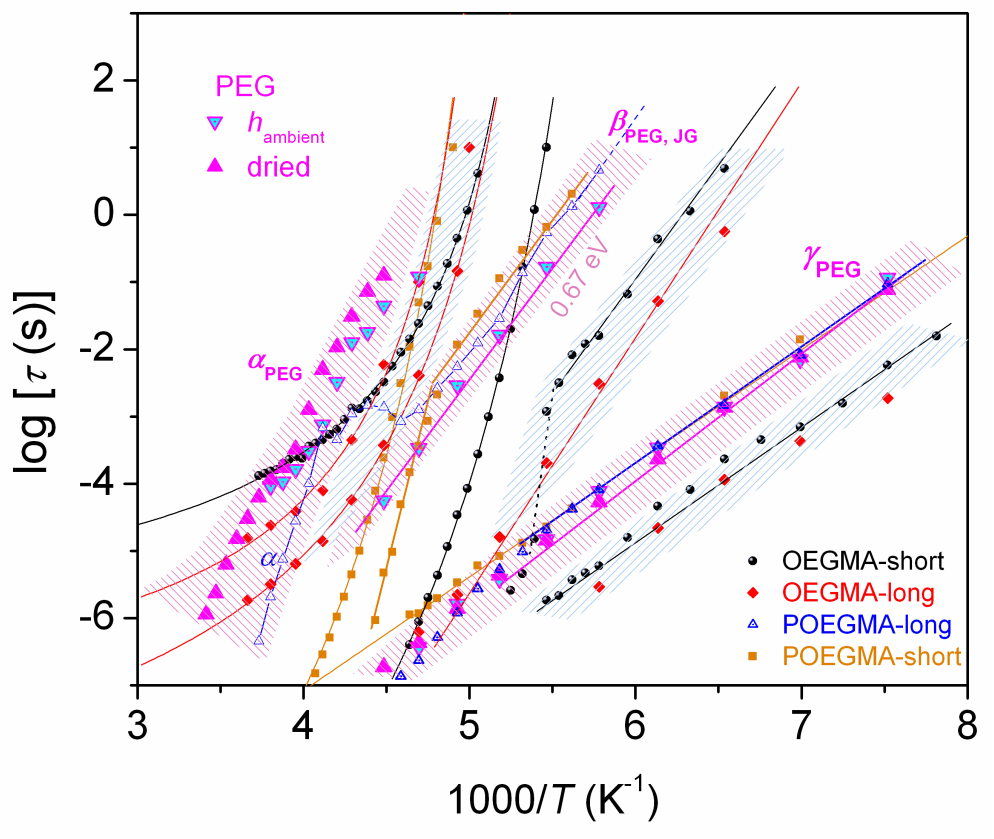

Figure S6. Arrhenius plots for all samples shown at a common plot, moreover, comparatively with data from the literature on poly(ethylene glycol) (PEG) -OH terminated with M_w ~36 kg/mol, at two states with respect to hydration level, namely with ambient hydration ($h_{ambient}$) and upon drying.

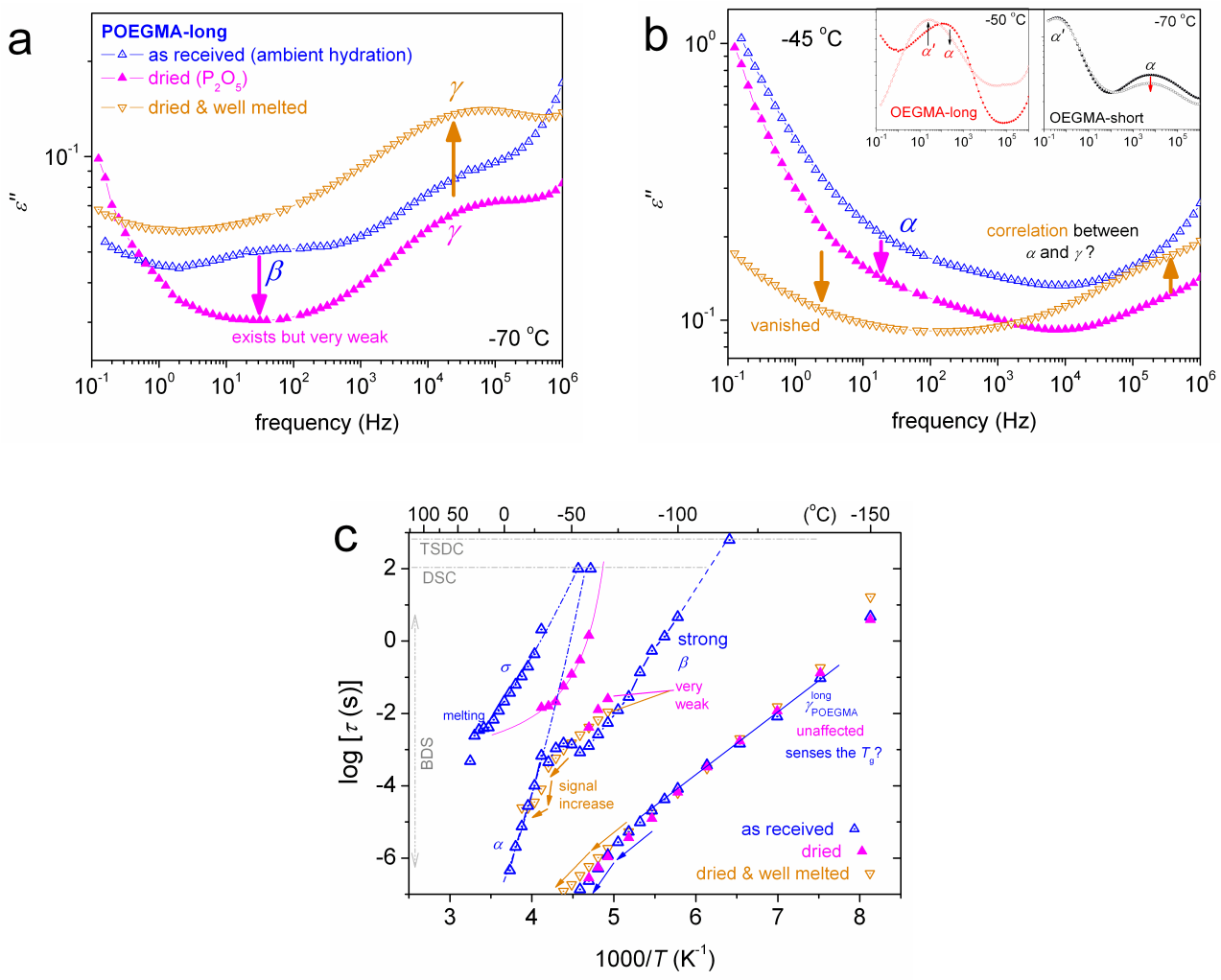

Figure S7. (a,b) BDS data of ε'' for POEGMA-long at (a) –70 °C and (b) –45 °C showing effects imposed by mild drying (solid magenta up-triangles) and, further, by melting well above T_m (open orange down-triangles). The two insets to (b) show respective changes on α and α' in OEGMA-long and OEGMA-short at –50 °C and –70 °C, respectively, between the 1st and 2nd BDS scans. (c) Comparative Arrhenius plots upon analysis for the aforementioned measurements.

S3. Additional TSDC data

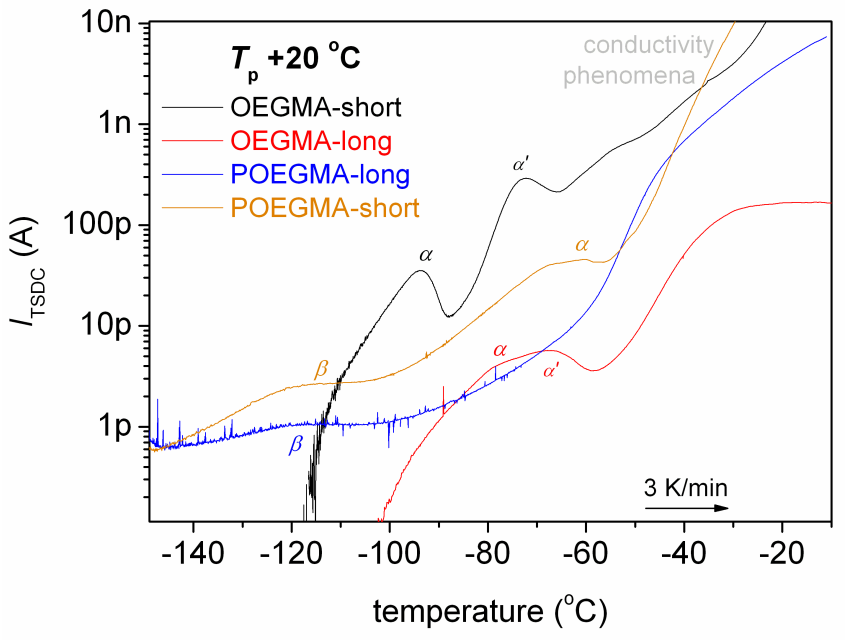

Figure S8. Comparative TSDC thermograms for all samples polarized at T_p = 20 °C. Indicated are the main relaxation peaks recorded.

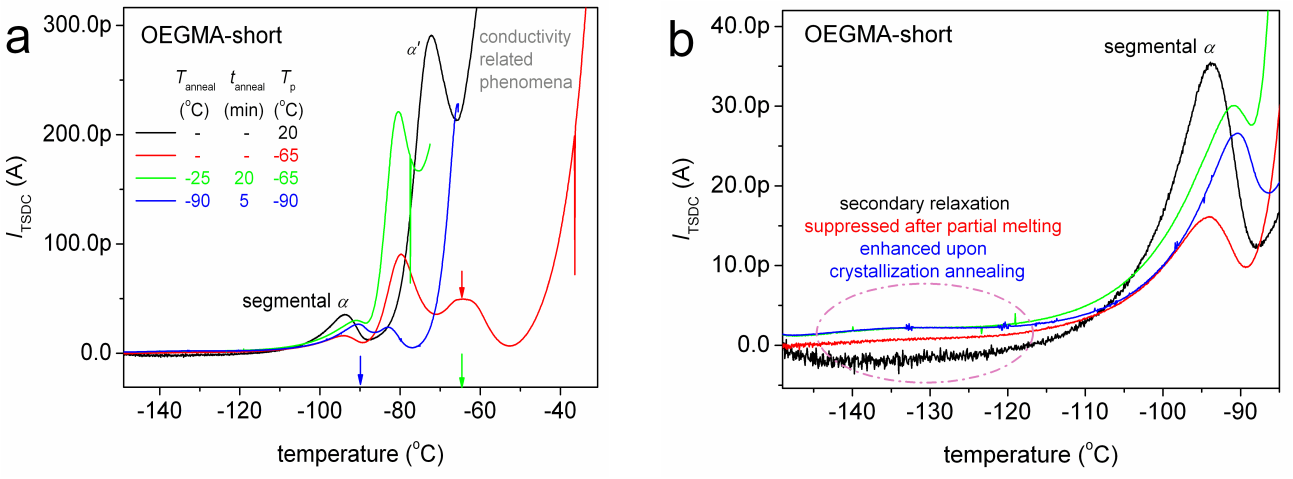

Figure S9. TSDC thermograms for OEGMA-short at different polarization and thermal treatments in (a) wide and (b) narrow temperature ranges.

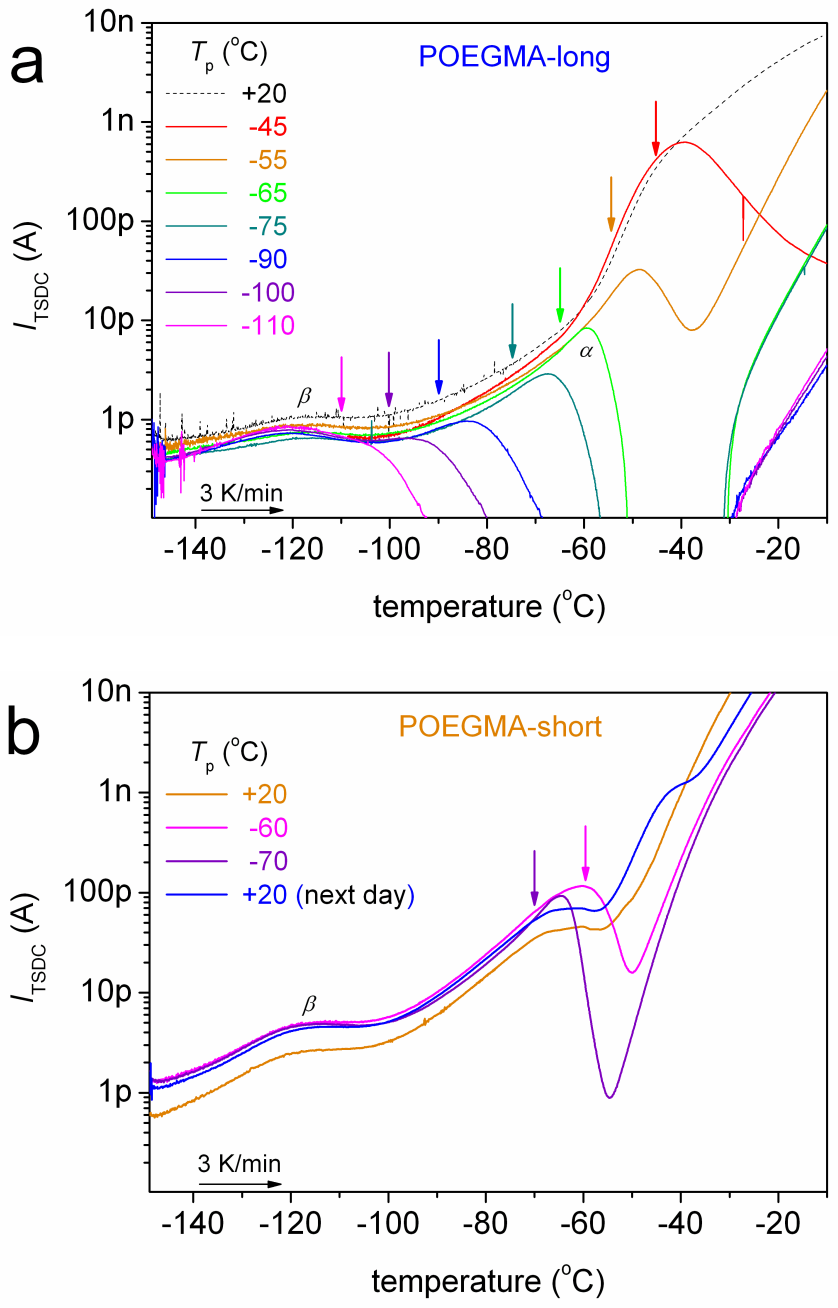

Figure S10. TSDC thermograms for (a) POEGMA-long and (b) POEGMA-short for different polarization temperatures (narrowing of the activation window).